The use of vapour phase ultra-violet spectroscopy for the analysis of arson accelerants in fire scene debris

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Abstract

A method has been developed for the analysis of arson accelerants in fire scene debris by vapour phase ultra-violet (UV) spectroscopy. The method is rapid, inexpensive, simple to use and is sufficiently sensitive and discriminating to be of use for the analysis of crime scene samples. Application to casework samples is described. On occasion, the method offers additional information to that which can be obtained by gas chromatography–flame ionisation detection (GC–FID) and gas chromatography–mass spectrometry (GC–MS) and represents a useful adjunct to these techniques. In addition, the method offers advantages where the use of GC–MS analysis of arson accelerants in fire scene debris is not a practical proposition. © 2001 Elsevier Science Ireland Ltd. All rights reserved.

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1. Introduction

The incidence and cost associated with fires has been increasing in the United States [1], the United Kingdom [2] and is recognised as an international problem [3–5]. In order to confirm that it can be determined whether or not a fire has been caused deliberately, it is necessary to examine the fire scene and on occasion collect material from the fire scene for analysis for the presence of flammable liquids. Whilst not always the case, deliberately set fires are indicated by the presence of flammable liquids at the identified origin of the fire [6].

The identification of such flammable liquids falls into four distinct phases, namely (i) collection of material from the fire scene, (ii) collection of flammable liquids from the debris in a form suitable for analysis, (iii) the analytical process itself and (iv) the interpretation and reporting of the findings. The first of the phases is often performed by someone other than a forensic scientist. Once the material is in the laboratory, there are a number of different methods that can be used to undertake the second and third phases ([7] and references contained therein). Identification of the flammable liquid is usually undertaken by gas chromatography–mass spectrometry (GC–MS). In some laboratory situations, it may not, however, be possible to operate GC–MS instruments, for example, where obtaining spare parts is difficult or where power supplies are intermittent. Whilst the operation of both types of instrument would be interrupted by the latter, a GC–MS instrument takes considerably longer than a ultra-violet (UV) spectrophotometer to return to full operational condition. Additionally, on occasion, the presence of one component of the accelerant can mask the presence of a second, especially, where the amount of one is greatly in excess of the other. This can lead to difficulties in interpretation of the GC–MS data.

Vapour phase UV spectroscopy is a well-established technique that can be used for the analysis of volatile components [8]. It is, therefore, well-suited to the analysis of components of flammable liquids which may have been used as arson accelerants. Indeed, one component of petrol, namely benzene, is used in the vapour phase as a standard for calibration of UV spectrophotometers [9]. In this paper, we describe the application of vapour phase UV spectroscopy to

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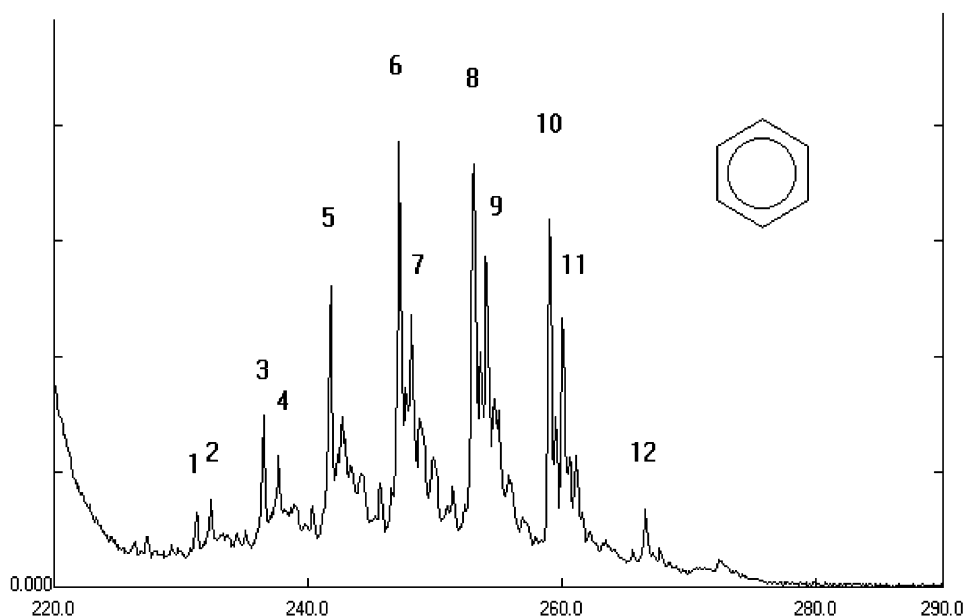[1] Present address: Anglia Polytechnic University, East Road, Cambridge, CB1 1PT, United Kingdom.

Fig. 1. Vapour phase ultra-violet (UV) spectrum of benzene. Absorption maxima are shown: (1) 231.4 nm; (2) 232.4 nm; (3) 236.4 nm; (4) 237.6 nm; (5) 241.7 nm; (6) 247.2 nm; (7) 248.2 nm; (8) 253.0 nm; (9) 254.0 nm; (10) 259.1 nm; (11) 260.1 nm; (12) 266.8 nm.

the analysis of arson accelerants. Comparison is made to GC–MS. The application of the method to two cases is described. The first example is an illustration of how the presence of aromatic hydrocarbons in petrol was masked by the great excess of paraffin in the flammable liquid, since the sample was extremely heavily weathered. The second example is one where different isomers of xylene were identified in a flammable liquid and hence identification of the flammable liquid was achieved using the vapour phase UV spectroscopy methodology.
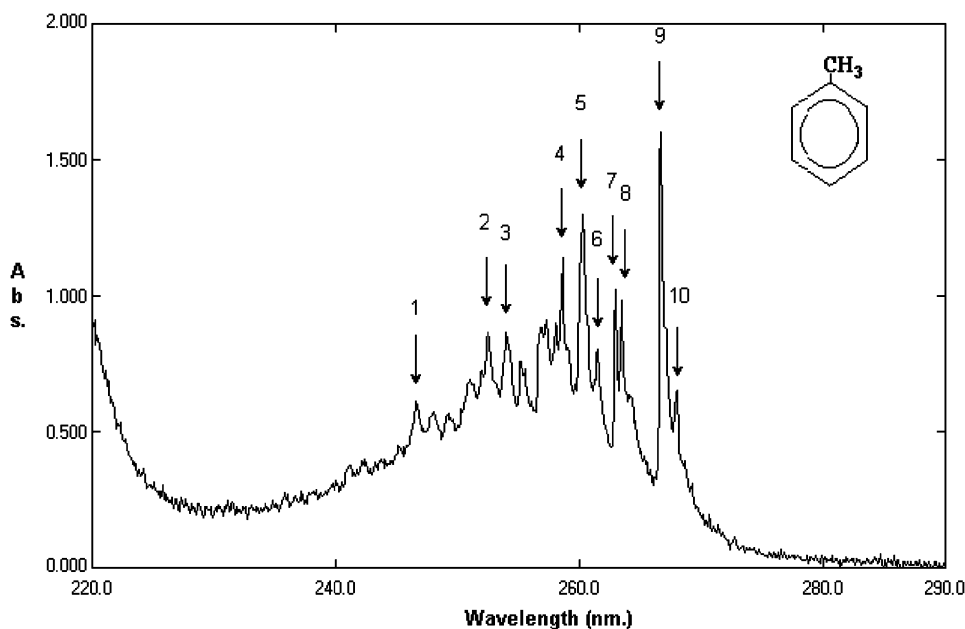

Fig. 2. Vapour phase UV spectrum of toluene. Absorption maxima are shown: (1) 246.5 nm; (2) 252.4 nm; (3) 253.9 nm; (4) 258.5 nm; (5) 260.3 nm; (6) 261.5 nm; (7) 263.0 nm; (8) 263.5 nm; (9) 266.8 nm; (10) 268.0 nm.
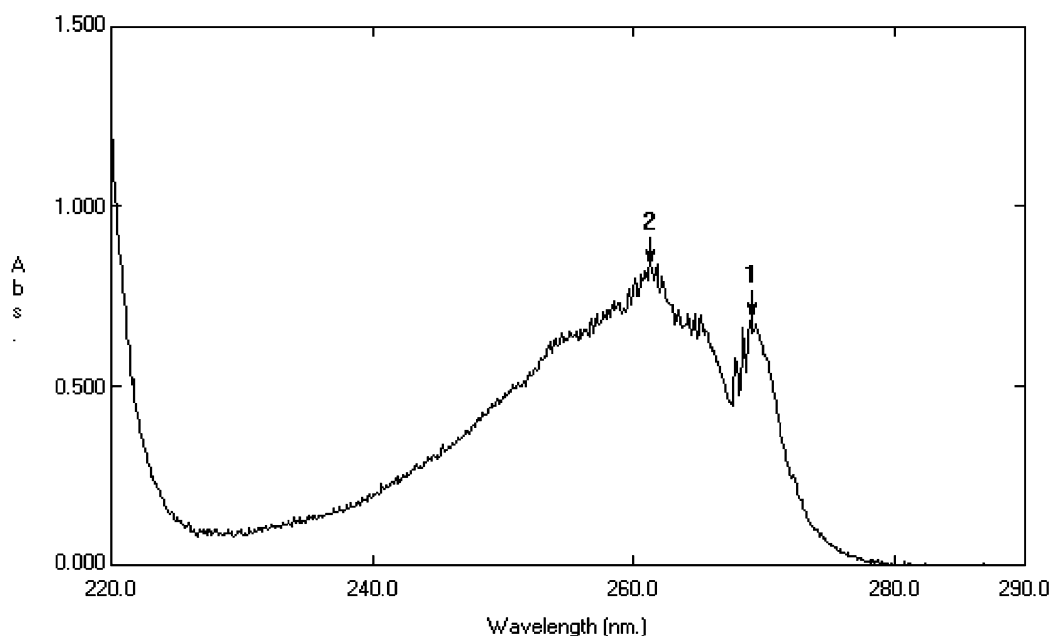
Fig. 3. Vapour phase UV spectrum of *o*-xylene. Absorption maxima are broad peaks at 1 and 2.

2. Materials and methods

2.1. Chemicals

All chemicals were obtained from Aldrich and were analytical reagent grade or better. Petrol, paraffin and diesel samples were obtained from petrol stations in Greater Indianapolis, IN, USA.

2.2. Treatment of casework materials for analysis

The method, recommended by the Bureau of Alcohol, Tobacco and Firearms, was used for casework material sampling [10]. The fire debris was placed in cleaned, unused metal cans at the fire scene. Where the samples had a noticeable odour, 1 ml of heated headspace vapour (60°C) was obtained through a small hole punched in the can and
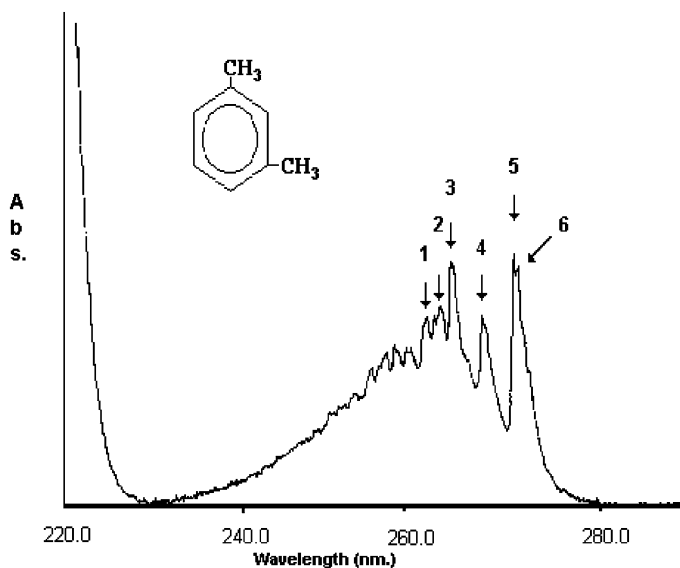

Fig. 4. Vapour phase UV spectrum of *m*-xylene. Absorption maxima are shown: (1) 260.8 nm; (2) 262.4 nm; (3) 263.6 nm; (4) 267.1 nm; (5) 270.5 nm; (6) 270.9 nm.
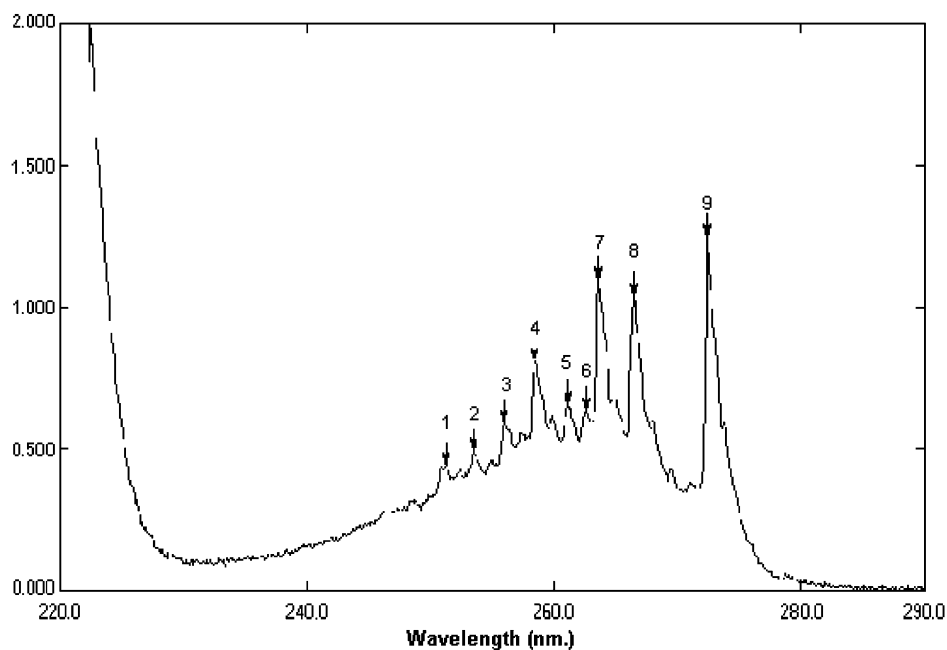
Fig. 5. Vapour phase UV spectrum of *p*-xylene. Absorption maxima are shown: (1) 251.2 nm; (2) 253.4 nm; (3) 255.9 nm; (4) 258.4 nm; (5) 261.1 nm; (6) 262.6 nm; (7) 263.6 nm; (8) 266.4 nm; (9) 272.4 nm.

analysed by gas chromatography with either flame ionisation or mass spectroscopic detection. Samples for vapour phase UV spectroscopy were obtained (see below) through the same punched hole. Where there was no noticeable odour, dynamic charcoal adsorption was employed. A small amount (circa 0.5 g) 50–200 mesh charcoal was packed into a Pasteur-pipette which was then connected to the can. The can was heated with a heating mantle and the resulting vapour drawn through the charcoal onto which the vapour sorbed. This was subsequently eluted with either *n*-hexane or CS_2 for vapour phase UV spectroscopy or for gas chromatographic analysis, respectively.
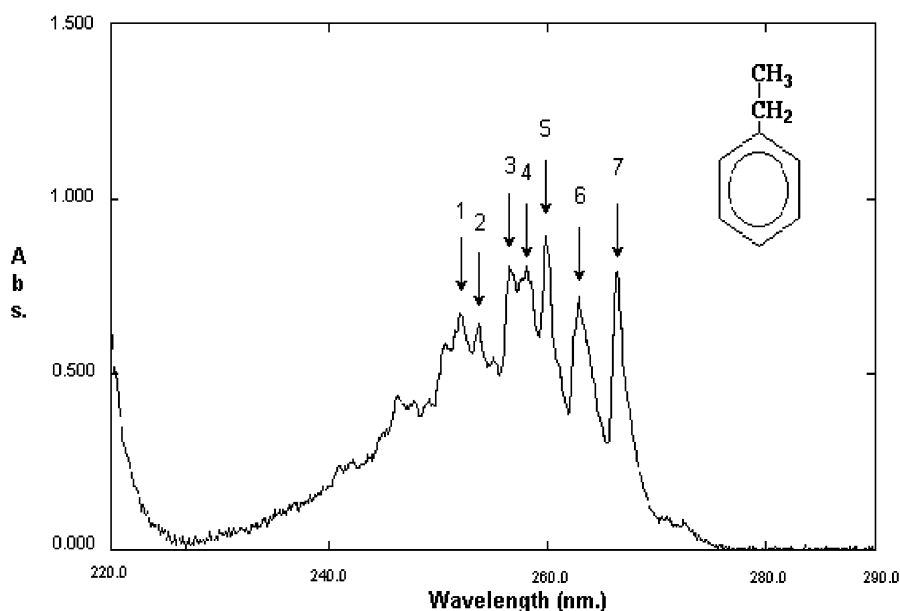

Fig. 6. Vapour phase UV spectrum of ethylbenzene. Absorption maxima are shown: (1) 252.0 nm; (2) 253.7 nm; (3) 256.6 nm; (4) 258.0 nm; (5) 259.9 nm; (6) 262.9 nm; (7) 266.5 nm.
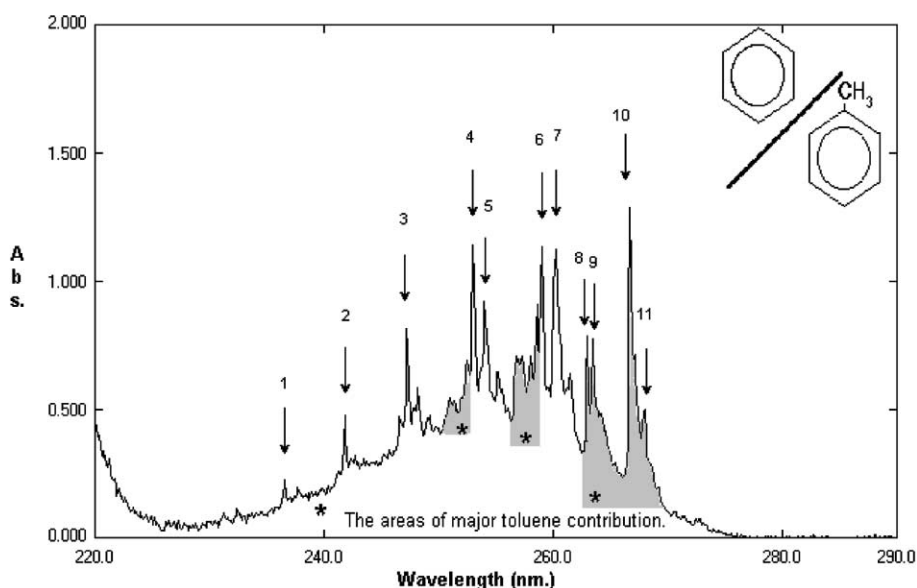
Fig. 7. Vapour phase UV spectrum of a mixture of 25% benzene–75% toluene. Absorption maxima are shown: (1) 236.6 nm; (2) 241.8 nm; (3) 247.2 nm; (4) 253.2 nm; (5) 254.0 nm; (6) 259.0 nm; (7) 260.2 nm; (8) 263.0 nm; (9) 263.5 nm; (10) 266.7 nm; (11) 268.0 nm.

2.3. Vapour phase UV spectroscopy

Spectroscopy was performed on a Shimadzu UV 260 spectrophotometer, modified to hold a 10 cm path length quartz cell. Spectra were obtained from either liquids (from both standards and casework materials), or from head space samples (from the casework materials). To obtain spectra from liquids (benzene, toluene, *o*-, *m*- and *p*-xylene, ethylbenzene,
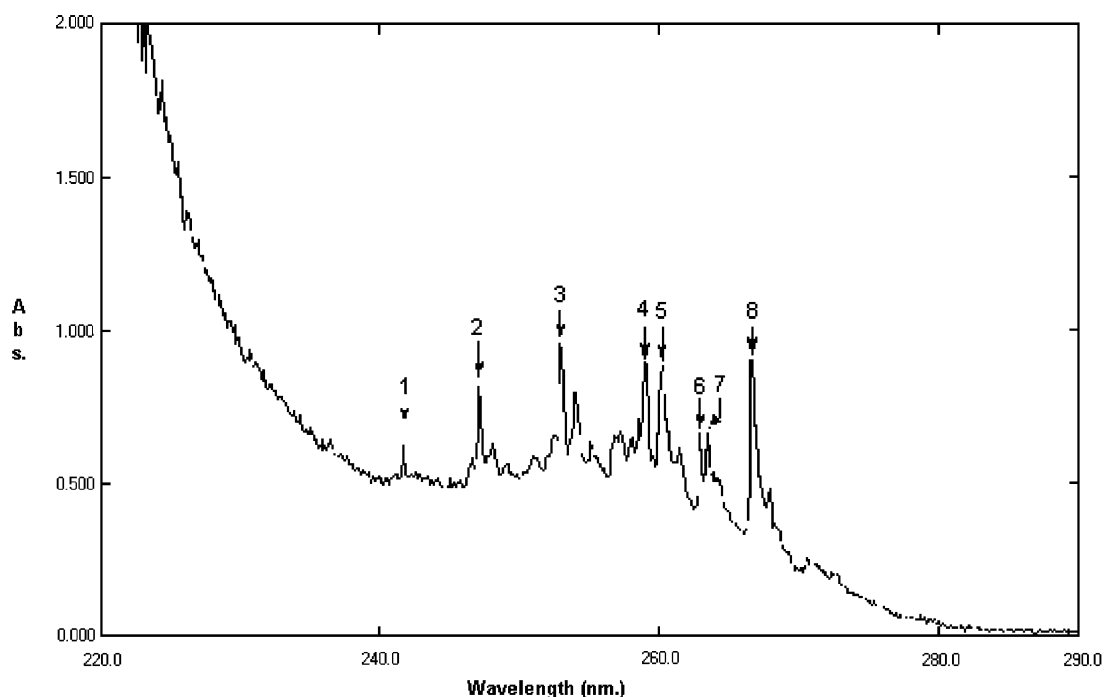

Fig. 8. Vapour phase UV spectrum of petrol (Amoco petrol Co.). Absorption maxima are shown: (1) 241.8 nm; (2) 247.2 nm; (3) 253.1 nm; (4) 259.0 nm; (5) 260.3 nm; (6) 263.0 nm; (7) 263.5 nm; (8) 266.7 nm.
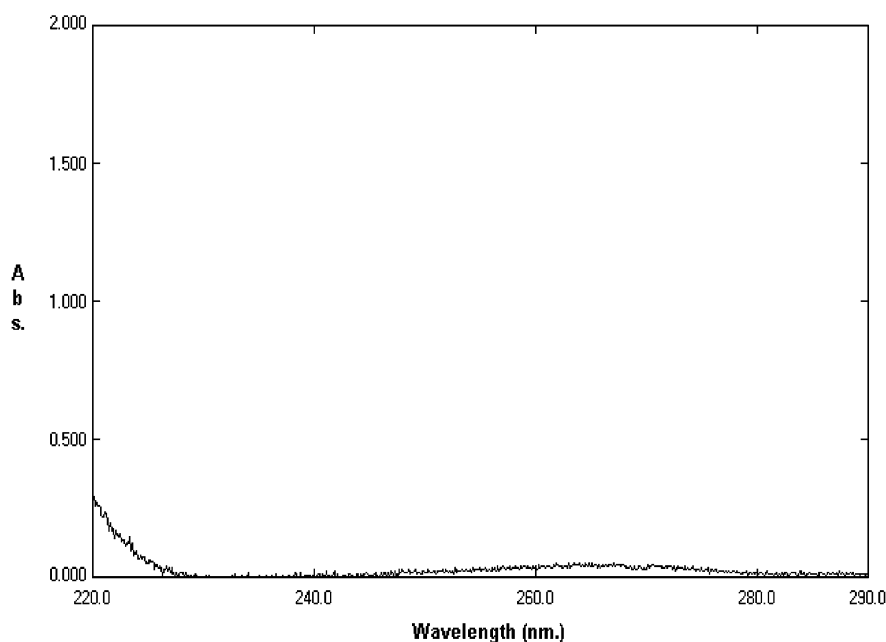
Fig. 9. Vapour phase UV spectrum of paraffin.

mixtures of these components representing petrol, paraffin, diesel, and liquid casework samples), between 1 and 25 μl liquid was placed in the vapour cell, depending on the volatility and extinction coefficients of the components of the mixture being analysed. The cell was sealed, the liquid was allowed to evaporate for 5 min at room temperature and the spectrum was recorded. For casework headspace samples, the cell was evacuated and a headspace sample from the fire debris drawn directly into the cell. Data was recorded over the wavelength range 230–280 nm, using a bandwidth of 0.2 nm.

2.4. Gas chromatography, flame ionisation detection

Chromatography was performed on an HP 5880A gas chromatograph fitted with a flame ionisation detector, using
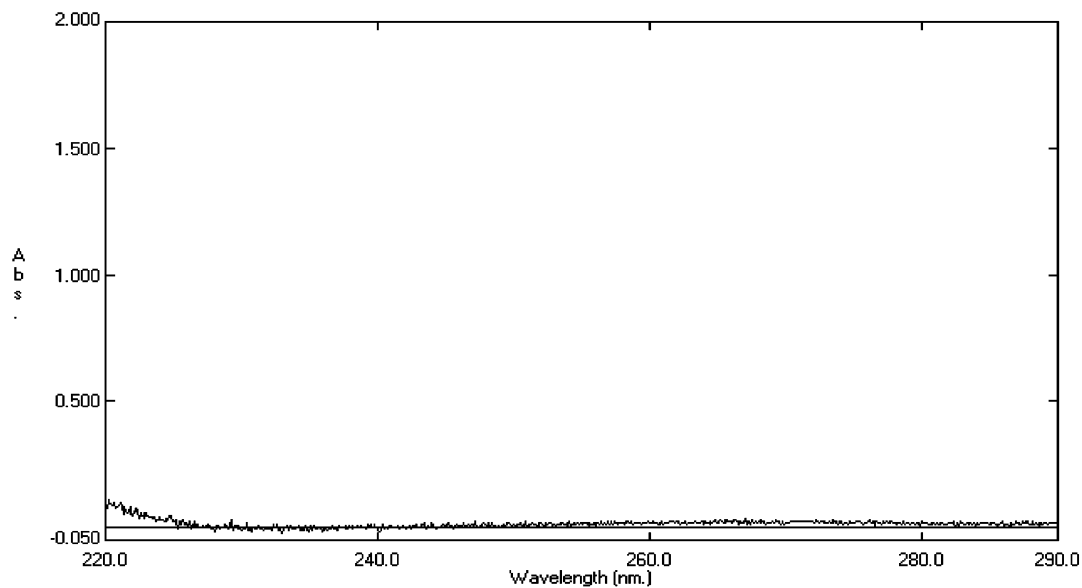

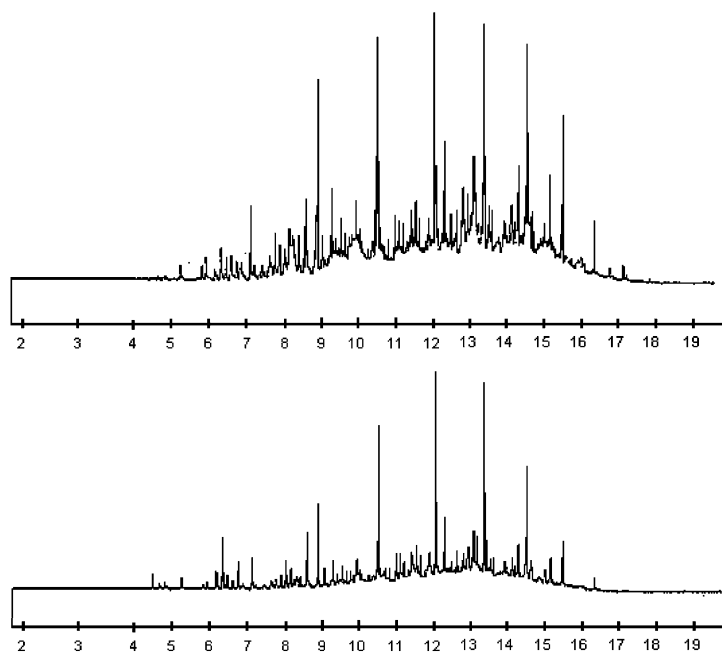Fig. 10. Vapour phase UV spectrum of diesel.

Fig. 11. Gas chromatogram (FID) of an arson accelerant detected in fire scene debris (top) and paraffin (bottom) obtained under identical conditions.

a split injection (split ratio 99:1) and an injection temperature of 265°C. The separation was effected on a J and W DB-1 column, 30 m × 0.25 mm i.d., $d_f = 0.25$ μm, using a three step temperature programme commencing at 40–65°C (0.5 min hold) at 7.5°C/min, (5 min hold) then to 135°C at 13°C/min, (1 min hold) lastly to 280°C at 18°C/min. Flame ionisation detection was employed at a temperature of 280°C. The carrier gas was nitrogen at a flow rate
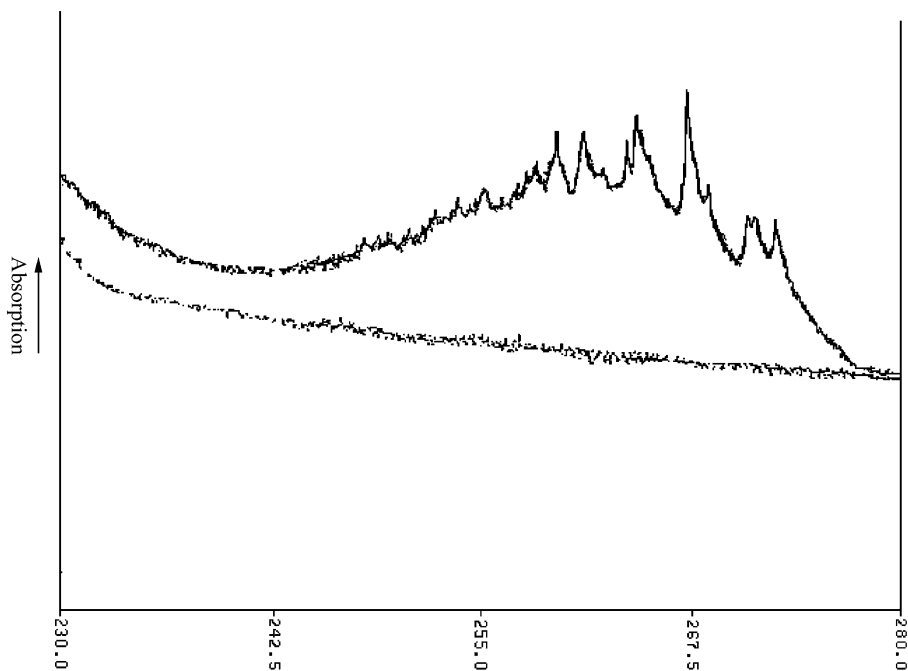

Fig. 12. Vapour phase UV spectrum of casework sample (top) and vapour cell blank (bottom).

of 1 ml/min. Pure liquids, mixtures of liquids and case-work samples were analysed as detailed in the results and discussion, with blanks carried out between each of the analyses.

2.5. Gas chromatography—mass spectroscopy

Chromatography was performed on a PE8500 gas chromatograph fitted with an ion trap detector, using a split injection (split ratio 90:1) and an injection temperature of 265°C. The separation was effected on a BP-5 column, $30 \, m \times 0.32$ mm i.d., $d_f = 0.5 \, \mu m$, using a temperature programme commencing at 40–280°C (0.5 min hold) at 10°C/min. Ion trap detection was employed with a transfer line and trap temperature of 280°C. The ion trap was programmed at a scan rate of 1 scan/s, with a mass range of 45–500 amu. The carrier gas was helium at a flow rate of 1 ml/min. Pure liquids, mixtures of liquids and casework samples were analysed as detailed in the results and discussion, with blanks carried out between each of the analyses.

3. Results and discussion

3.1. Vapour phase UV spectroscopy of aromatic hydrocarbons and arson accelerants

The vapour phase UV spectra of exemplar aromatic hydrocarbons and common arson accelerants are shown below (Figs. 1–10). A database for 52 aromatic hydrocarbons and fuels has been established. The full data set is available from the authors. The aromatic hydrocarbons exemplified here have distinctive vapour phase UV spectra, with the exception of o-xylene. The paraffin and diesel samples do not have vapour phase absorption spectra. This is due to their composition, which is principally straight and branched chain alkanes. Petrol, in contrast, has a significant absorption spectrum, due to the aromatic hydrocarbon content. Additionally, it can be seen from the mixture of benzene and toluene (Fig. 7), used here as an example, that the absorption spectra are additive and individual components of mixtures can be identified.

The minimum amount of material which can be used to produce a spectrum varies with compound. In the case of the
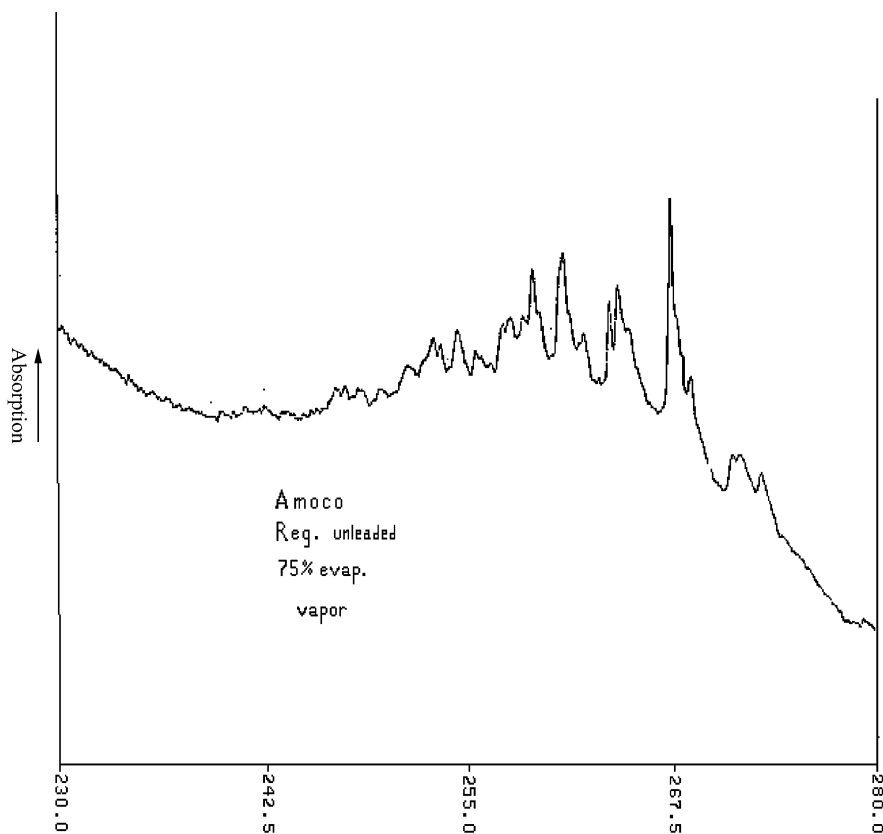

Fig. 13. Vapour phase UV spectrum of Amoco regular unleaded petrol 75% weathered (evaporated).

simple, volatile aromatic hydrocarbons, as little as 1 μl is required. A spectrum can be produced from 2 μl petrol. This allows this methodology to be used for arson accelerant analysis where aromatic hydrocarbons are thought to be present.

3.2. Casework example 1: determination of petrol in a mixture of arson accelerants

A sample of fire debris was submitted to the laboratory for analysis. The volatile components were collected using the adsorption–elution technique described above and subjected to GC–FID analysis. The resulting data are shown in Fig. 11. It was clear from the data that paraffin was present, but that another component was present too. One possibility was that petrol had been mixed with the paraffin (in this case, determined empirically to be 1–10 parts by volume). This is a well-known arson accelerant mixture. However, a technique other than GC–FID was required to determine whether or not this was the case. The material was, therefore, subjected to vapour phase UV spectroscopy to determine whether the aromatic hydrocarbons typical of petrol were

present (Fig. 12). The benzene component had evaporated, but the toluene and xylene components were clearly evident. The spectrum obtained suggested that heavily weathered (75%) petrol might be present in the sample, in addition to the paraffin. Subsequent vapour phase UV spectroscopy of weathered petrol (Fig. 13) yielded an almost identical spectrum.

In order to confirm that the accelerant was indeed a heavily weathered petrol paraffin mixture, a sample of weathered petrol and paraffin was prepared and subjected to GC–FID (Fig. 14). From the data generated by vapour phase UV spectroscopy and GC–FID, it is clear that the arson accelerant was a mixture of heavily weathered petrol and paraffin.

3.3. Casework example 2: identification of a xylene-based cleaning fluid

Fire scene debris was submitted to the laboratory for analysis, along with a bottle of liquid called "Goof Off" seized from a defendant. This latter is a xylene-based cleaning fluid, manufactured from technical grade xylenes.
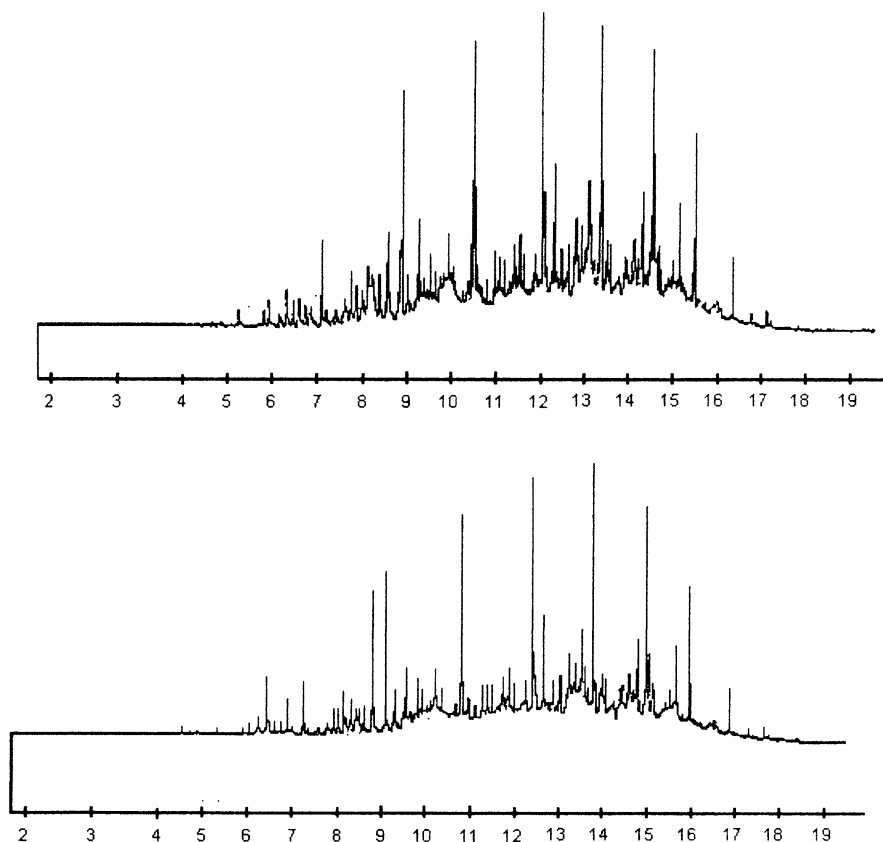

Fig. 14. GC–FID chromatogram of arson accelerant recovered from fire scene debris (top) and 75% weathered petrol–paraffin mixture (bottom).
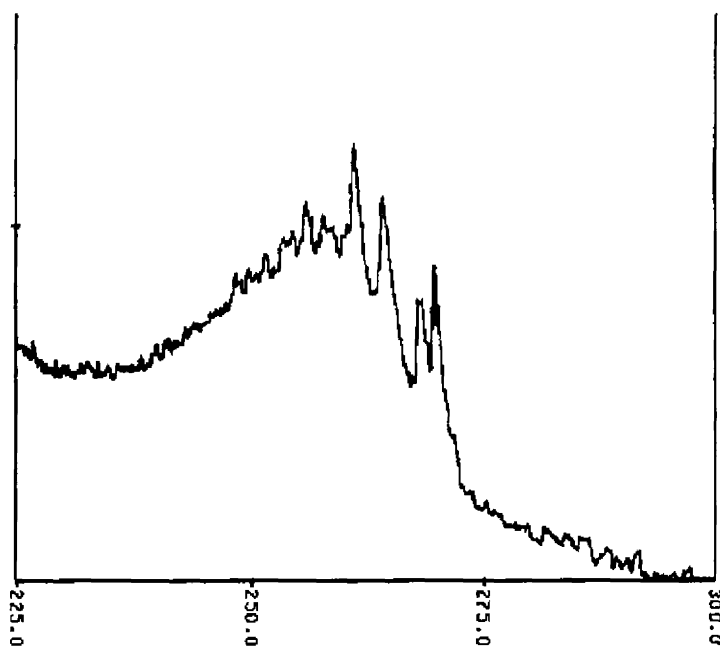
Fig. 15. Vapour phase UV spectrum of liquid recovered from fire scene debris.

Such mixtures cannot be readily analysed by GC–MS since in the system described *m*- and *p*-xylene co-elute and the mass spectra cannot be differentiated.

The materials were subjected to vapour phase UV spectroscopy. The spectra obtained from the sample from the fire scene (Fig. 15) and the sample of "Goof off" seized from the defendant's truck (Fig. 16) were identical to a mixture of 75% *m*-xylene–25% *p*-xylene (Fig. 17). The method could, therefore, be used to determine the ratios of the different isomers of xylene which could not be determined by GC–MS.
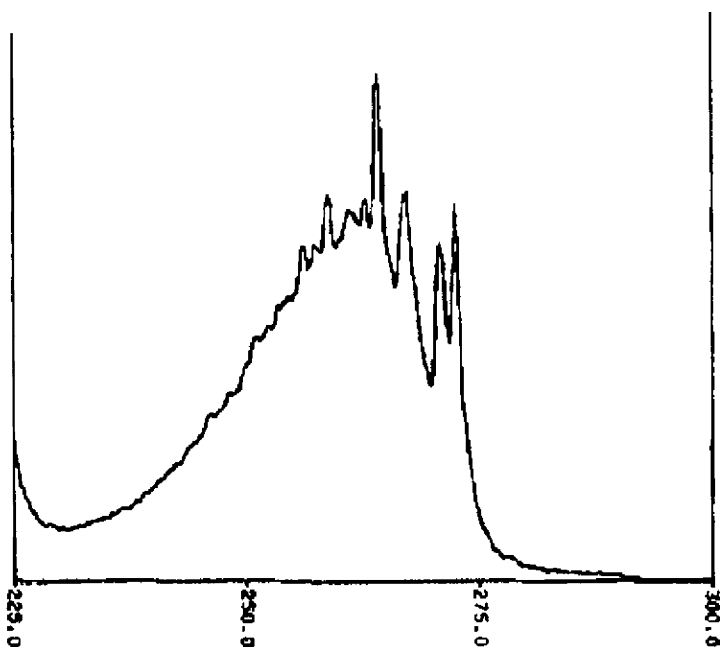

Fig. 16. Vapour phase UV spectrum of liquid recovered from suspect's truck, labelled "Goof off".
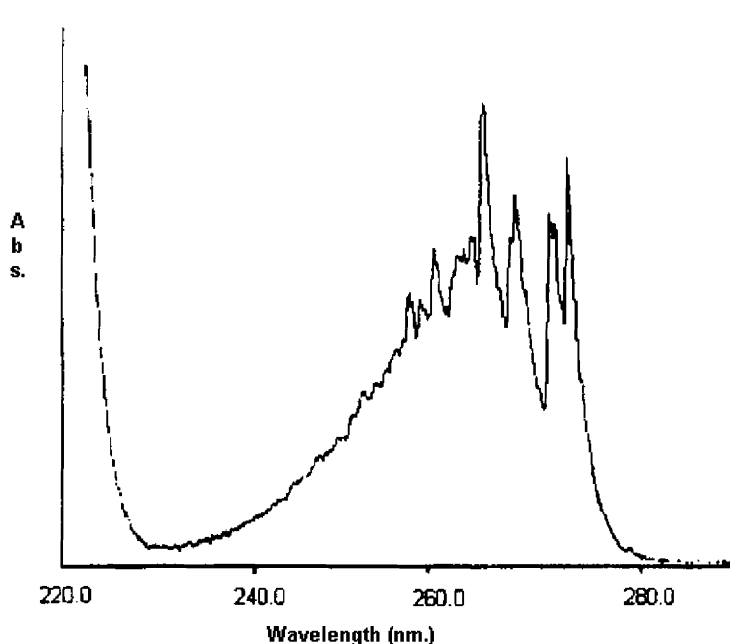
A
b
s.

220.0   240.0   260.0   280.0

Wavelength (nm.)

Fig. 17. Vapour phase UV spectrum of a mixture of 75% *m*-xylene–25% *p*-xylene, as found in technical grade xylene and in ''Goof Off''.

4. Conclusions

The method of vapour phase UV spectroscopy can be used for the analysis of arson accelerants in fire scene debris. There are inherent difficulties with the method in that it cannot be used to analyse alkanes or polycyclic aromatic hydrocarbons. Whilst vapour phase UV spectroscopy has a number of disadvantages and not intended to replace GC–MS, on occasion, it offers advantages over GC–MS, especially, when one components of a mixture, which contains aromatic hydrocarbons is masked by the presence of a much greater amount of other accelerants.

Further, the method can be used with GC–FID, for example, to confirm that accelerants containing aromatic hydrocarbons, for example, petrol are present in a sample. This is especially useful in situations, where GC–MS cannot be used. Further, the UV spectrophotometer itself is less expensive than a GC–MS and the analysis time is considerably shorter allowing higher sample throughput. This method provides a useful adjunct to currently existing techniques for the analysis of arson accelerants.

Acknowledgements

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